1103. *The Stereochemically Inert Lone Pair? A Speculation on the Bonding in* $SbCl_6^{3-}$, $SeBr_6^{2-}$, $TeBr_6^{2-}$, IF_6^-, XeF_6, *etc.*

By D. S. URCH.

The nature of the bonding in hexa-halogen complexes of non-transition elements is considered. It is suggested that if the ns orbital (a_{1g}) of the central atom plays little part in bonding then an extra pair of electrons may be accommodated in the a_{1g} antibonding molecular orbital, without distorting the O_h structure. It is also argued that electrons in such an ns orbital will decrease the effective electronegativity of the central atom so that nd orbitals can be better used in bonding. This is most important for halogens less electronegative than fluorine. Those conditions that favour the formation of hexa-halogen complexes *with* a lone pair will also favour such complexes having a regular octahedral structure. The factors that affect the bonding and stability of complexes with and without a lone pair and the factors that determine which type of complex will be formed with a given halogen are also discussed.

THE stereochemistry of most non-transition-element compounds seems to be governed by electrostatic repulsions between pairs of valence electrons.[1] Possible exceptions to this rule are the hexa-halogen complex anions formed by selenium(IV), tellurium(IV), and polonium(IV). Such evidence as is available (X-ray powder diffraction photographs[2-4] and nuclear quadrupole resonance[5]) suggests that these anions are regular octahedra and that the lone-pair has no stereochemical effect. Other simple compounds in which the same problem may exist are $AsCl_6^{3-}$, $AsBr_6^{3-}$, $SbCl_6^{3-}$, $SbBr_6^{3-}$, $BiCl_6^{3-}$, $BiBr_6^{3-}$, BiI_6^{3-}, IF_6^-, and XeF_6. This Paper discusses the bonding in such compounds, to see if the regular octahedral configuration (point group O_h)[6] is possible, and, if so, what conditions favour its formation.

The Table shows how XL_6 and $:XL_6$ complexes are distributed amongst the non-transition elements for each of the four halogens. The factors that may be important in determining whether an element will form a hexa-halogen complex and, if so, of what type it will be, will now be considered.

Valency-shell s-*Orbital* (ns).—Two factors control the efficiency of bonding between the X s orbital and the ligands' a_{1g} molecular orbital, namely, the energy difference between the orbitals and the size of the resonance integral.[7] An estimate of the former orbitals may be determined from the Figure in which approximate atomic orbital binding energies, calculated from atomic spectra[8] using Jaffé's method,[9] are presented.

The resonance integral may be assumed approximately proportional to the overlap integral.[10] For a given set of ligand orbitals the a_{1g} molecular orbital will be more or less constant but the s orbital of X will change in character on going down any group in the Periodic Table. As the principal quantum number (n) increases so will the number of nodal surfaces ($n-1$) in the s orbital.[11] Whilst the effective nuclear charge might well be sufficient to remove these nodes from the bonding region, still their effect will be greatly to reduce the amplitude

[1] Gillespie and Nyholm, *Quart. Rev.*, 1957, **9**, 339; Gillespie, *Canad. J. Chem.*, 1960, **38**, 818; 1961, **39**, 318; Gillespie, *J.*, 1963, 4672, 4679.
[2] Hoard and Bickinson, *Z. Krist.*, 1933, **84**, 436; Engel, *ibid.*, 1935, **90**, 341.
[3] Bagnell, d'Eye, and Freeman, *J.*, (a) 1955, 2320; (b) 1955, 3959; (c) 1956, 3385.
[4] Manojlović, *Bull. Inst. Nuclear Sci. "Boris Kidrich" (Belgrade)*, 1956, **6**, 194.
[5] Nakamura, Ito, and Knbo, *J. Amer. Chem. Soc.*, 1962, **84**, 163.
[6] Mulliken, *Phys. Rev.*, 1933, **43**, 279.
[7] Coulson, "Valence," Oxford Univ. Press, Oxford, 2nd edn., 1961, p. 74.
[8] Moore, "Tables of Atomic Energy Levels" (Nat. Bureau of Standards Circular No. 467), U.S. Govt. Printing Office, Washington D.C., U.S.A., 1949—52.
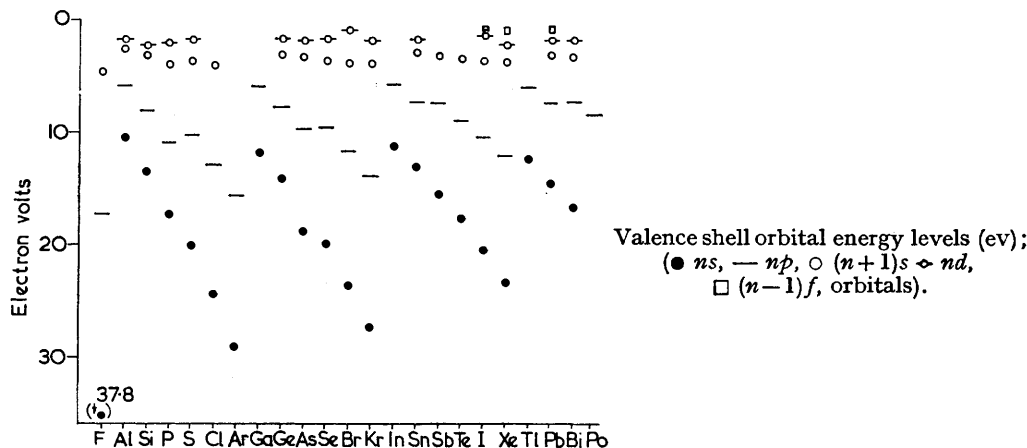[9] Jaffé, *J. Chem. Educ.*, 1956, **33**, 25.
[10] Chirgwin and Coulson, *Proc. Roy. Soc.*, 1950, *A*, **201**, 196.
[11] Pauling and Wilson, "Introduction to Quantum Mechanics," McGraw-Hill, New York, 1935, pp. 134, 142.

of the ns wave function in the bonding region. The a_{1g} overlap integral will therefore become smaller on going down any group. The chemistry[12] of the elements of the fourth row and more especially of the lower rows may be understood if it is assumed that this nodal effect is important for $n = 4$ or 5 and becomes more important for $n > 5$. It cannot be argued that the increasing inertness of the s orbital is due to the s orbital's becoming more tightly bound, since, as can be seen from the Figure, this is not so.

The most tightly bound s orbitals in any row lie to the right. Inefficient a_{1g} bonding is therefore expected in this region; to the left this type of bonding will contribute increasingly to the stability of the complex. A reduction in the efficiency of a_{1g} bonding is also to be expected on descending any group since this is associated with a reduction in the overlap integral. The combination of these effects will result in a_{1g} bonding being at a nadir in the bottom right-hand corner of the Periodic Table.

Valence shell orbital energy levels (ev);
($\bullet$ ns, — np, $\circ$ $(n+1)s$ $\diamond$ nd,
$\square$ $(n-1)f$, orbitals).

$(n+1)s$ *Orbital.*—Associated with the a_{1g} orbital there will be an antibonding a_{1g}* orbital. This will be only slightly antibonding when the interaction between the ns and ligand a_{1g} orbital is small. Under these conditions if the a_{1g}* orbital were to house an extra pair of electrons they would detract little from the stability of the complex and would be found almost entirely on the ligands. Electron repulsions between such a_{1g}* electrons and the six other pairs would be small so that stable :XL_6 complexes of octahedral symmetry could be formed.

The effect of the loosely bound $(n+1)s$ orbital on X has so far been ignored. That such interaction might be important has been suggested by Beach[13] and has been used to rationalise the formation of kryptates ($KrO_4{}^{2-}$, *i.e.*, :XL_4).[14] It seems reasonable to suppose that the $(n+1)s$ orbital should become more compact and more tightly bound when the X atom is surrounded by strongly electronegative ligands, as has been suggested for nd orbitals.[15] Even if this effect were small the energy difference between the ligand a_{1g} m.o. and the X ns orbital is often greater than between the ligand m.o. and the X $(n+1)s$ orbital so that appreciable interaction might be expected. The effect of including the $(n+1)s$ orbital would then be to turn the a_{1g}* m.o. from being slightly antibonding into a bonding orbital (relative to the ligand orbitals). This would provide an explanation for a curious feature of the chemistry of :XL_6 complexes. The extra pair of electrons not only seems quite tightly bound, but in

[12] (*a*) Sidgwick, "The Chemical Elements and their Compounds," Oxford Univ. Press, Oxford, 1950; (*b*) Cotton and Wilkinson, "Advanced Inorganic Chemistry," Wiley, New York, 1962.

[13] Beach, reported by Pauling in "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, New York, 3rd edn., 1960, p. 251.

[14] Urch, *Nature*, 1964, **202**, 403.

[15] Moffit, *Proc. Roy. Soc.*, 1950, *A*, **200**, 409; Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, 332; Craig and Magnusson, *J.*, 1956, 4895; Craig and Zauli, *J. Chem. Phys.*, 1962, **37**, 601, 609.

many cases seems necessary for the compounds' existence. Salts of $TeCl_6^{2-}$, $TeBr_6^{2-}$, and TeI_6^{2-}, for example, have been prepared[16] even with strongly polar cations such as lithium and magnesium and the corresponding uncharged compounds ($TeCl_6$, etc.) are unknown.

Electronegativity Difference.—Tables of electronegatives, calculated from various recipes, are given in the literature (*e.g.*, ref. 12*b*, p. 92). The electronegativity difference between a halogen and a given element will decrease in the order fluorine, chlorine, bromine, iodine. The power to polarise the X atom, and thus confer bonding potential upon its d orbitals,[15] will decrease in the same order. The largest range of XL_6 complexes will therefore be found when the ligand is fluorine and the smallest when the ligand is iodine.

An interesting situation arises if X's s orbital is more tightly bound than the ligand orbitals and plays little part in bonding with them. Two electrons in this s orbital will screen the electrons in p orbitals from the nucleus. Since these orbitals now experience a reduced effective nuclear charge, they are more easily polarised by electron attracting ligands. This in turn exposes the d orbitals to an increased nuclear charge and will permit them to play a greater part in bonding. This is equivalent to saying the electronegativity of the p electrons would be decreased by two tightly bound s electrons. An electron pair in a suitable s orbital will therefore produce an increased electronegativity difference between a given atom and a halogen. This effect is especially important for halogens less electronegative than fluorine.

Crystal Forces.—In moving to the left across any row a complex of the type XL_6 or $:XL_6$ becomes more negatively charged. Since the size of the anion will alter little, the surface density of charge will increase. This will increase crystal forces between the cations and the complex anions. If the cohesive forces ("covalent bonding") in a complex are weak then the isoelectronic anion in the group to the left might well be unstable in a comparable crystal environment. Octahedral co-ordination of X by L might, however, be retained by two means. Either the bonding in XL_6 or $:XL_6$ becomes more truly ionic or polymeric anions are formed in which the charge per XL_6 (or $:XL_6$) unit is reduced. In the first case the complex anion no longer exists and in the second the ligand sharing must necessarily produce some distortion of the monomeric XL_6 or $:XL_6$ structure.

DISCUSSION

It will be convenient to divide X, s-orbital, and ligand-orbital interaction into three main classes and to discuss within each the effect of moving from right to left across any row.

(1) The X s orbital is more tightly bound than the ligand orbitals and interaction with the ligand orbitals is small. (1*A*) The electronegativity difference between X and L is small and even the presence of shielding electrons in the s orbital does not enable the ligands to confer bonding potential upon the d orbitals. Neither XL_6 nor $:XL_6$ is formed. (1*B*) d Orbitals can be used in bonding if electrons are present in s orbital. Therefore complexes of the type $:XL_6$ can be formed but XL_6 cannot. (1*C*) As in (1*B*), but the $:XL_6$ anion now carries a larger negative charge, so that is unstable in a crystal. Octahedral covalent co-ordination of X by L may be retained only if polymeric anions are formed.

(2) The s orbital is more tightly bound than the ligand p orbitals but the interaction between these orbitals is no longer small. The a_{1g} bonding orbital in the complex will therefore have much ($> 50\%$) X s character but electrons in this orbital will not shield the X nucleus as efficiently as in (1). Thus the effective electronegatives of X and $:X$ will be similar and ligands that can utilise the d orbitals in one case will be able to do so in the other. (2*A*) The ligands are not able to confer bonding potential upon d orbitals. Therefore neither XL_6 nor $:XL_6$ complexes are formed. (2*B*) d Orbitals can be used for bonding. Both XL_6 and $:XL_6$ type complexes will be formed. For the same X atom $:XL_6$ will carry two more negative charges than XL_6 and will therefore be more subject to crystal instability than XL_6. Octahedral co-ordination of $:X$ may be retained in a variety of ways. (2*C*) Polymeric anions based on $:XL_6$ alone or both $:XL_6$ and XL_6. (2*D*) Crystals may contain both $:XL_6$ and XL_6 anions.

[16] Zara, *Acta Salmanticensia Ser. Cienc.*, 1961, **3**, No. 1, p. 9; Frias, *ibid.*, p. 31; Angoso y Catalina, *ibid.*, p. 77 (Chem. Abs., 1962, **57**, 12092—3).

If the s orbital interacts very strongly with the ligand orbitals then the :XL_6 complexes will probably distort from the regular octahedral configuration.

(3) When the s orbital is less bonding than the ligand p orbitals or when the s orbital interacts strongly with the ligand orbitals, electrons in the bonding a_{1g} orbital of XL_6 (or :XL_6) do not screen the X p orbitals from the X nucleus. Thus :XL_6 complexes will not be formed. (3A) Electronegativity difference between X and L is not sufficient to permit the use of d orbitals in bonding. Therefore XL_6 is not formed. (3B) Moving to the left the electronegativity difference is increased. d Orbitals can now be used in bonding and XL_6 is formed. (3C) Further to the left the anion charge of XL_6 is such that it is unstable in a crystal environment. Compounds containing discrete XL_6 anions are therefore unknown, but octahedral co-ordination of X might still be found in polymeric anions. (3D) XL_6 is not known or the bonding is wholly ionic. The general operation of these effects is indicated in the Table and cases of special interest are considered below.

Fluorides.

Row ↓	Group →	III	IV	V	VI	VII	VIII
2	XL_6	AlF_6^{3-a} 3B, C	SiF_6^{2-a} 3B	PF_6^{-a} 3B	SF_6^b 3B	— 3A	— 2A
	:XL_6	—	—	—	—	—	—
3	XL_6	GaF_6^{3-c} 3B, C	GeF_6^{2-a} 3B	AsF_6^{-d} 3B	SeF_6^b 3B(2B?)	— 1B	— 1A or B?
	:XL_6	—	—	—	$SeF_6^{2-?e}$	BrF_6^{-f}	(KrF$_6$)
4	XL_6	InF_6^{3-g} 3B, C	SnF_6^{2-e} 3B	SbF_6^{-a} 3B(2B?)	TeF_6^b 2B	— 1B	— 1B
	:XL_6	—	—	$SbF_6^{3-?h}$	TeF_6^{2-i}	$IF_6^{-f,j}$	XeF_6^k
5	XL_6	TlF_6^{3-g} 3B, C	PbF_6^{2-l} 3B, C	BiF_6^{-m} 3B	(PoF$_6$) 2B	(AtF$_6^+$) 1B or 2B?	— 1B
	:XL_6	—	—^{n}	—	(PoF$_6^{2-}$)	(AtF$_6^-$)	(RnF$_6$)

Chlorides.

Row ↓	Group →	III	IV	V	VI	VII
2	XL_6	— 3D	—^{o} 3D	PCl_6^{-p} 3B	— 2A	— 1A
	:XL_6	—	—	—	—	—
3	XL_6	— 3D	$GeCl_6^{2-q}$ 3B	(AsCl$_6^-$) 1C(B?) (2C?)	— 1B	— 1A
	:XL_6	—	—	$AsCl_6^{3-r}$	$SeCl_6^{2-a}$	—
4	XL_6	$InCl_6^{3-e}$ 3B	$SnCl_6^{2-a}$ 3B	$SbCl_6^{-e,s}$ 2B, C	— 1B	— 1A
	:XL_6	—	—	$SbCl_6^{3-s,t}$	$TeCl_6^{2-a}$	—
5	XL_6	$TlCl_6^{3-a,u}$ 3B, C	$PbCl_6^{2-a,v}$ 2B, C	— 1B	— 1B	— 1A(1B?)
	:XL_6	—	$PbCl_6^{4-v,w}$	$BiCl_6^{3-c,x}$	$PoCl_6^{2-y}$	(AtCl$_6^-$?)

Bromides.

Row ↓	Group →	III	IV	V	VI	VII
2	XL_6	— 3D	— 3D	PBr_6^{-z} 3B, D	— 2A	— 1A
	:XL_6	—	—	—	—	—
3	XL_6	— 3D	— 3D	(AsBr$_6^-$)^{aa} 1B, C (2C?)	— 1B	— 1A
	:XL_6	—	—	$AsBr_6^{3-aa,bb}$	$SeBr_6^{2-a}$	—
4	XL_6	$InBr_6^{3-e}$ 3B	$SnBr_6^{2-a}$ 3B	$SbBr_6^{-s,cc}$ 2B, C	— 1B	— 1A
	:XL_6	—	—	$SbBr_6^{3-s,cc}$	$TeBr_6^{2-dd}$	—
5	XL_6	$TlBr_6^{3-e}$ 3B	— 1B	— 1B	— 1B	— 1A
	:XL_6	—	$PbBr_6^{4-ee}$	$BiBr_6^{3-c,ff}$	$PoBr_6^{2-dd}$	—

Iodides.

Row	Group	III	IV	V	VI	VII
2		3A	3A	2A	1A	1A
	XL6	—	—	—	—	—
3		3A	3A	1C	1A	1A
	:XL6			AsI_6^{3-}		
	XL6	—	SnI_6^{2-}[a]	—	—	—
4		3D	3B	1C	1B	1A
	:XL6	—	—	SbI_6^{3-}[ll]	TeI_6^{2-}[ii,ff]	—
	XL6	TlI_6^{3-}[e]	—	—	—	—
5		3B				
	:XL6	3B	1B	1B, C?	1B	1A
		—	PbI_6^{4-}[w]	BiI_6^{3-}[kk,hh]	PoI_6^{2-}[ii]	—

[a] Ref. 29. [b] Braune and Knoke, *Z. phys. Chem. (Leipzig)*, 1933, **B21**, 297. [c] Ref. 12. [d] Roof, *Acta Cryst.*, 1955, **8**, 739; Ibers, *ibid.*, 1956, **9**, 967. [e] Ref. 22. [f] Bode and Klesper, *Z. anorg. Chem.*, 1961, **313**, 161. [g] Bode and Voss, *Z. anorg. Chem.*, 1957, **290**, 1. [h] Ref. 25. [i] Emeléus and Sharp, *J.*, 1949, 2206. [k] Ref. 18. [l] Hoppe and Blinne, *Z. anorg. chem.*, 1958, **293**, 251. [m] Fischer and Rudzitis, *J. Amer. Chem. Soc.*, 1959, **81**, 6375. [n] Ref. 17. [o] Ref. 26. [p] Clark, Powell, and Wells, *J.*, 1942, 642. [q] Laubengayer, Billings, and Newkirk, *J. Amer. Chem. Soc.*, 1940, **62**, 546; Waddington and Klanberg, *Naturwiss.*, 1959, **46**, 578; Udovenko and Fialkov, *Russ. J. Inorg. Chem.*, 1960, **5**, 728. [r] Hoard and Goldstein, *J. Chem. Phys.*, 1935, **3**, 117; Andrieth, Long, and Edwards, *J. Amer. Chem. Soc.*, 1936, **58**, 428. [s] (a) K. A. Jensen, *Z. anorg. Chem.*, 1937, **232**, 193; (b) A. T. Jensen and Rasmussen, *Acta. Chem. Scand.*, 1955, **9**, 708. [t] Jandar and Immig, *Z. anorg. Chem.*, 1937, **233**, 302. [u] Watanabé, Atoji, and Okazaki, *Acta, Cryst.*, 1950, **3**, 405. [v] Ref. 32. [w] Ref. 31a. [x] Ref. 32b. [y] Ref. 3a. [z] Kolditz and Feltz, *Z. anorg. Chem.*, 1957, **293**, 155. [aa] Ref. 27. [bb] Ref. 28. [cc] Petzold, *Z. anorg. Chem.*, 1933, **215**, 92; Brauer and Schnell, *ibid.*, 1956, **283**, 49. [dd] Ref. 3b. [ee] Ref. 20a. [ff] Ref. 20b. [gg] Ref. 28. [hh] Ref. 34. [ii] Ref. 3c. [jj] Ref. 4. [kk] Ref. 31b.

TeF_6^{2-}, IF_6^-, XeF_6. The ionisation potential of the p orbital of fluorine is much larger than that of the other halogens (17·4 ev) so that strong a_{1g} interaction occurs with even tightly bound s orbitals and $:XF_6$ complexes are rare. Those elements that do form such complexes will be found in the bottom right-hand corner of the Periodic Table where a_{1g} bonding is weakest (*i.e.*, Br, Kr, Te, I, Xe, Po, At, and Rn). The s orbital of tellurium has an ionisation potential comparable to that of the p orbital of fluorine so that if TeF_6^{2-} is formed it might well be distorted, but the tendency to distort will decrease in the series TeF_6^{2-}, IF_6^-, XeF_6. KIF_6 has been reported[17] not to be isomorphous with $KSbF_6$ but whether the IF_6^- anion is or is not a regular octahedron has not yet been established. Again, XeF_6 is more likely to have O_h symmetry than IF_6^-. If it is distorted then the distortions will be slight and even small (non-ionic) crystal forces might well cause the molecules to adopt a regular shape. Solid XeF_6 undergoes a phase change and becomes coloured just below its m. p.; this transition might be due to a change of shape of the XeF_6 molecules.

The bonding is XeF_6 has had much comment. Gillespie's[18a] electron-pair repulsion model forecasts that XeF_6 will be distorted. The method implicitly assumes that s, p, and d orbitals contribute comparably to the bonding. A contrary view has been suggested by Rundle[18b] and also by Pitzer[18c] who use only xenon p orbitals in their molecular orbital models; this leads to O_h symmetry for XeF_6. The model suggested here lies between these extremes. The contribution of the xenon $6s$ orbital to bonding is small, but the shape of the molecule is determined by how small it is. Xenon p orbitals play the most important role in bonding but the empty $5d$ orbitals strengthen the xenon–fluorine σ bonds by interacting with filled fluorine molecular orbitals that are non-bonding (e_g) in the Rundle and Hinze–Pitzer models.

The increasing ionisation potential of the $5s$ electron is reflected in the chemistry of tellurium, iodine, and xenon. Tellurium readily forms compounds in which the s orbital bonds well, TeF_6, TeF_7^-, and TeF_8^{2-}(?).[19] Iodine forms IF_7, showing that the s orbital here also

[17] Bartlett, *Endeavour*, 1964, **23**, 6.
[18] (a), (b), (c); H. H. Hyman (Ed.) "Noble-Gas Compounds," Univ. of Chicago Press, Chicago, U.S.A., 1963; (b) Rundle, *J. Amer. Chem. Soc.*, 1963, **85**, 112; (c) Pitzer, *Science*, 1963, **139**, 414.
[19] Muetterties, *J. Amer. Chem. Soc.*, 1957, **79**, 1004.

bonds with fluorine, but not as much as in tellurium since IF_6^- is, and IF_6^+ and IF_8^- are not, known. A continuation of these trends should be observed in xenon. XeF_6 is known but XeF_7^+ and XeF_8 are probably incapable of existence (save perhaps at very low temperatures).

Oxygen, whilst less electron-attracting than fluorine, can behave as if it were a more electronegative ligand, sometimes evoking a higher formal valency than fluorine. With chlorine (which has a relatively tightly bound $3s$ orbital) oxygen can form ClO_4^- (VII), but fluorine only ClF_5 (V).[20] This effect has been ascribed[21] to oxygen's ability to form additional π-bonds with the central atom. In the fourth row $4f$ orbitals might well be used (or less probably $5d$) in π-bonding with oxygen ligands in $Sn(OH)_6^{2-}$, $Sb(OH)_6^-$, $Te(OH)_6$, IO_6^{5-}, and XeO_6^{4-}, The π-bonding would stabilise those anions in which the σ bonds are weakened by the lack of effective a_{1g} bonding. Since fluorine forms π-bonds less readily than oxygen the presence of octavalent xenon in XeO_6^{4-} does not anticipate the formation of XeF_8.

SeF_6^{2-}, TeF_6^{2-}, PoF_6, PoF_6^{2-}. Salts of composition M_2SeF_6[22] have been reported, from solutions of selenium tetrafluoride in hydrofluoric acid, but no structural determinations have been made to decide whether these salts contain SeF_6^{2-} anions. Rather unstable fluorotellurites[23] have also been prepared. The possible occurrence of these compounds is in accordance with the transition from class 1 to class 2 on descending a group. Further, it is to be expected that polonium will form PoF_6 and also salts of PoF_6^{2-}.

PbF_6^{4-}. Many salts of Pb^{2+} have been made in which the lead atom is surrounded by an octahedron of fluorine atoms.[24] Whilst bond lengths have not yet been determined the lead–fluorine bonding is probably mostly ionic, and no PbF_6^{4-} complex anion can be said to exist.

SbF_6^{3-} has been suggested[25] as an intermediate in the polarographic reduction of SbF_6^-; no salts are known.

$SiCl_6^{2-}$. Attempts to produce salts of this anion,[26] even with the most suitable chlorine-coated cations (PCl_4^+, $AsCl_4^+$), have been to no avail. Devin and Perrot claim evidence for a complex $SiCl_4,2NOCl$ from freezing-point data, but nothing is known of its structure.

$AsBr_6^-$, $AsBr_6^{3-}$. The complexes containing bromine and arsenic are many and curious.[27,28] No structural determinations have been made. The formulae of some complexes seem to invoke the presence of quinquevalent arsenic but these compounds might contain only arsenic(III) and $-Br_3$ ligands. However Petzold,[27] in the analysis of $(Me_4N)_3As_2Br_{11}$, has shown the presence of both quinque- and ter-valent arsenic.

$AsCl_6^-$, $AsCl_6^{3-}$. If $As_2Br_{11}^{3-}$ does contain quinquevalent arsenic it should be possible to prepare similar compounds with chlorine ligands, since chlorine is more electronegative than bromine.

$PbCl_6^{2-}$, $PbCl_6^{4-}$. Hexachloroplumbates[16,29,30] are well known but salts of $PbCl_6^{4-}$ have also been reported.[31] Mori[32a] has described the preparation of diamagnetic $[Co^{III}(NH_3)_6]PbCl_6$ which probably contains lead in both valency states (cf. Rb_2SbCl_6) and is isomorphous with $[Co^{III}(NH_3)_6]BiCl_6$.[32b]

AsI_3, SbI_3, BiI_3. In these solids the central atom is octahedrally co-ordinated by six

[20] Smith, *Science*, 1963, **141**, 1039.
[21] Urch, *J. Inorg. Nuclear Chem.*, 1963, **25**, 771.
[22] Clifford, Beachell, and Jack, *J. Inorg. Nuclear Chem.*, 1957, **5**, 57, 71.
[23] Aynsley and Hetherington, *J.*, 1953, 2802.
[24] Schmitz-Dumont and Bergerhoff, *Z. anorg. Chem.*, 1956, **283**, 314; **284**, 10.
[25] Pavlov, *Zhur. neorg. Khim.*, 1958, **3**, 2099.
[26] Devin and Perrot, *Compt. rend.*, 1958, **246**, 950; Waddington and Klanberg, *J.*, 1960, 2329, 2332; Kolditz and Schmidt, *Z. anorg. Chem.*, 1958, **296**, 188; Nisel'son and Seryakov, *Russ. J. Inorg. Chem.*, 1960, **5**, 548.
[27] Petzold, *Z. anorg. Chem.*, 1933, **214**, 365.
[28] Popov, *Zhur. obshchei Khim.*, 1949, **19**, 47.
[29] Wells, "Structural Inorganic Chemistry," Oxford Univ. Press, Oxford, 3rd edn., 1962.
[30] Wycoff, "Crystal Structures," Interscience, New York, 1948—60, vol. III.
[31] Mellor "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, London, (a) vol. 7, 1927; (b) vol. 9, 1929.
[32] (a) Mori, *Bull. Chem. Soc. Japan*, 1951, **24**, 285; (b) Atoji and Watanabé, *J. Chem. Phys.*, 1952, **20**, 1045.

iodine atoms and each iodine is bound to two arsenic, antimony, or bismuth atoms.[33] The structure is therefore a polymer based on :XL_6 units.

Probably the iodides (as distinct from the other trihalides) (cf. ref. 34) adopt this configuration because the p orbitals of iodine are the most diffuse and least tightly bound of all the halogens. a_{1g} bonding is weak, and a class (1) situation is generated.

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[33] Kojima, Tsukada, Ogawa, Shimauchi, and Abe, *J. Phys. Soc. Japan*, 1954, **9**, 805; Barnes and Bray, *J. Chem. Phys.*, 1955, **23**, 1177.
[34] Cavalca, Nardelli, and Braibanti, *Gazzetta*, 1955, **85**, 1239.